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Template Synthesis of the Trinuclear Cobalt(III) Complex with Diarylimidazole-Based Ligands: Synthesis and Properties

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Abstract—The trinuclear cobalt(III) complex $[(Bipy)_5Co_3(L)_2](Cl)_3$ (**I**) is synthesized by the template reaction of 2,2'-(1*H*-imidazole-4,5-diyl)bis(4-ethylphenol) (L) and bis(2,2-bipyridine)cobalt(II) dichloride in the presence of diazabicycloundecene. The complex is isolated in the individual state and characterized by elemental analysis, cyclic voltammetry, UV-VIS spectroscopy, and X-ray diffraction (XRD) (CIF file CCDC no. 2201135). According to the obtained data, the cobalt ions in trinuclear complex **I** have the oxidation state +3, and the complex formation occurs with the oxidation of the initial cobalt(II) ions.

Keywords: polynuclear cobalt complexes, redox-active ligands, XRD, cyclic voltammetry, UV-VIS spectroscopy

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INTRODUCTION

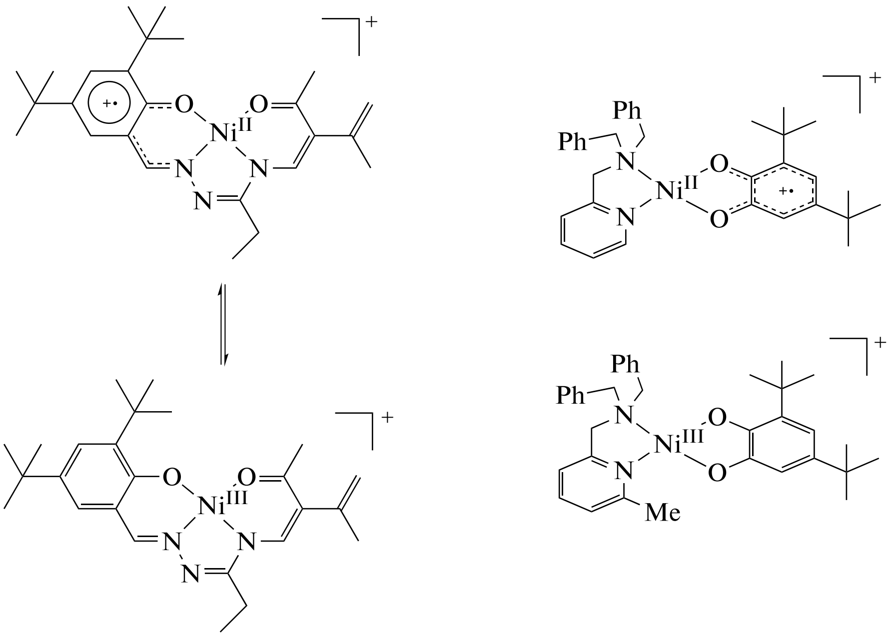
Advanced concepts on the fabrication of devices of superdense information storage, molecular switchers, and other materials are based on the development of molecular systems able to the intramolecular electron transfer [1, 2]. These systems are exemplified by the transition metal complexes (including polynuclear complexes) containing at least two redox centers: the metal ion [3] and/or redox-active ligand [4] bound via a bridge due to which the metal—metal interaction or the transfer of an electron of the ligand to the metal becomes possible [5].

The dioxalene metal complexes [6, 7] or ligands of the Salen type [8] (*N*,*N*'-bis(salicylidene)ethylenediamine) with the N_2O_2 donor set are often chosen as the ligand to provide the intramolecular electron transfer, since they are often prone to valence tautomerism between the catecholate and *o*-semiquinone metal complexes [8, 9]. Similar compounds can give different products depending on the external action, for example, temperature [1, 8] or ligand geometry (Scheme 1) [10], similarly to the transition metal complexes that undergo spin transition with changing temperature, pressure, or light irradiation [11, 12].

Various functional complexes with Salen ligands have been synthesized to date by complex formation with the corresponding metal sources [13, 14]. However, there are few published examples of the binuclear and trinuclear systems containing dioxolene fragments [15].

The development of the chemistry of stable phenoxy radical complexes impelled the study of their coordination behavior, including the cases where they are components of polynuclear heterovalence complexes [1]. The most part of these efforts was concentrated on bridged nitrogen-containing heterocyclic ligands, which, as it is well known, favor the interaction between metal atoms via the π system of the ligand. 2,2-Bipyrimidine [16], 1,2,5-oxadiazole and 1,2,5-thiadiazole [17], imidazole [18], and others [19] were used as these bridging ligands.

We have recently synthesized the 2,2'-(1*H*-imidazole-4,5-diyl)bis(4-ethylphenol) ligand (L) with the N_2O_2 donor set and showed a possibility of occurring ligand-centered oxidation processes in the binuclear complexes based on this ligand [20]. In this work, an earlier unknown trinuclear complex $[(Bipy)_5Co_3(L)_2](Cl)_3$ (**I**) was synthesized and its electrochemical and optical properties were examined.



Scheme 1.

EXPERIMENTAL

All synthetic procedures were carried out in air using commercially available organic solvents distilled under an argon atmosphere. Complex $(Bipy)_2CoCl_2$ [21] and ligand L [20] were synthesized using previously described procedures. Analyses to carbon, nitrogen, and hydrogen were conducted on a CarloErba microanalyzer (model 1106). The UV-VIS spectra of the compounds were recorded in an acetonitrile solution at room temperature on a Shimadzu UV-2600i two-beam spectrophotometer in the wavelength range from 240 to 1400 nm.

Synthesis of $[(Bipy)_5Co_3(L)_2](Cl)_3$ (I). A solution of ligand L (0.1 g, 0.00032 mol) in methanol (15 mL) was prepared in a 50-mL round-bottom flask, and diazabicycloundecene (DBU) (0.17 mL, 0.0011 mol) was added dropwise. The reaction mixture was stirred at room temperature for 5 min. Then a solution of *cis*-bis(2,2-bipyridine)dichlorocobalt(II) (0.30 g, 0.00068 mol) in methanol (10 mL) was added, and the mixture was stirred at room temperature for 4 h. The resulting dark green solution was evaporated, and the residue was dissolved in a mixture of acetonitrile and dichloromethane in a ratio of 2 : 1 (vol/vol) and filtered. Dark green crystals of the trinuclear cobalt(III) complex were formed upon the slow evaporation of solvents at room temperature in air. The yield was 0.36 g.

For $C_{88}H_{74}N_{14}O_4Cl_3Co_3$

Anal. calcd., %	C, 63.11	H, 4.45	N, 11.71
Found, %	C, 63.40	H, 4.36	N, 12.07

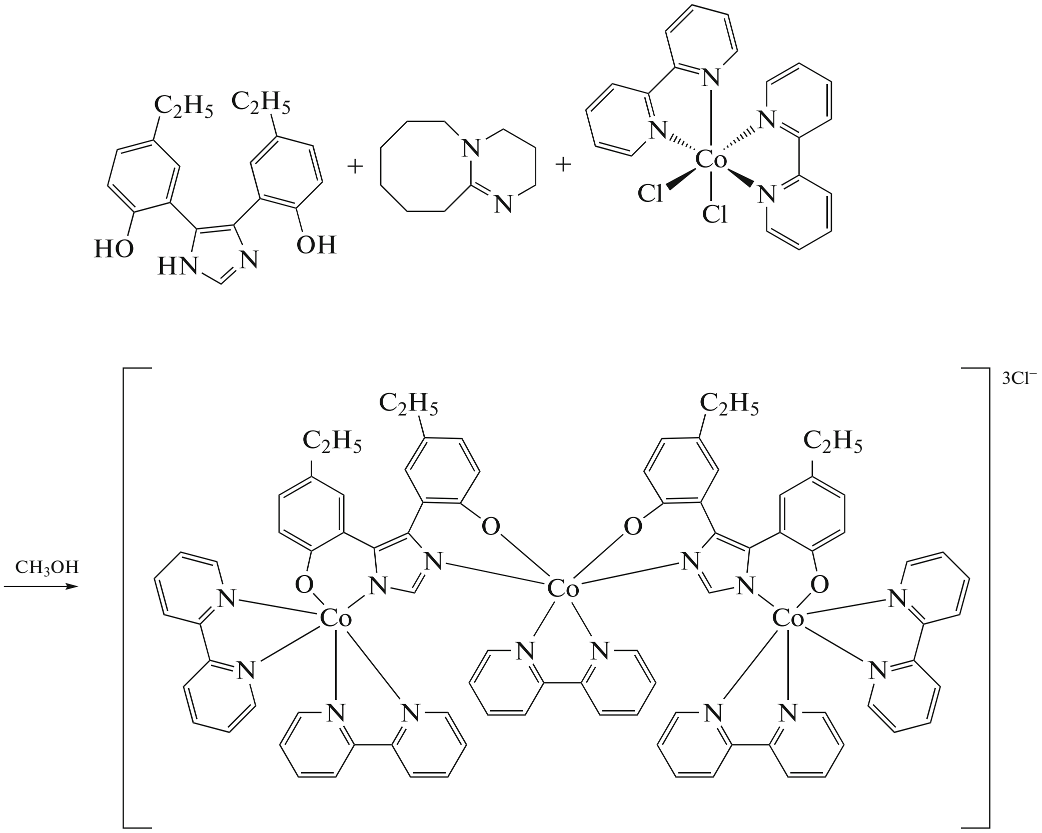
XRD of single crystals of complex **I** was carried out on a Bruker Quest D8 diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structure was solved using the ShelXT program [22] and refined by full-matrix least squares using the Olex2 program [23] in the anisotropic approximation for F^2_{hkl}. The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. Disordered molecules of the solvent (acetonitrile) were described as a diffuse contribution to the total scattering using the Solvent Mask option implemented in the Olex2 program [23]. The main crystallographic data and structure refinement parameters are given in Table 1.

The structural data for complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2201135; http://www.ccdc.cam.ac.uk/).

Cyclic voltammetry (CV). Cyclic voltammograms were recorded on an Autolab PGSTAT128N potentiostat/galvanostat equipped with the NOVA 2.0 software in a standard three-electrode cell with a glassy carbon working electrode 3 mm in diameter, a platinum wire counter electrode, and an Ag/AgCl reference electrode in a saturated KCl solution. A 0.1 M solution of $TBAPF_6$ in acetonitrile served as the electrolyte. All current–voltage curves were measured at a potential sweep rate of 100 mV/s. Prior to each experiment, the studied solution was purged with argon for 5 min to remove dissolved air, and the working electrode was thoroughly polished. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The template reaction of cobalt(II) bis(2,2-bipyridine)dichloride ($Bipy_2CoCl_2$) and 4,5-disubstituted imidazole (L) [20] in the presence of the DBU base (Scheme 2) afforded the trinuclear complex $[(Bipy)_5Co_3(L)_2](Cl)_3$ (**I**) in which all cobalt ions have the oxidation state +3, indicating that this transformation involves oxidation processes. Such a base as DBU was chosen owing to its low coordination ability. The repeated synthesis of this complex in an inert atmosphere of a glove box gives an analogous reaction product. The metal to ligand ratio in this reaction was 2 : 1, since the initial purpose was to synthesize the binuclear cobalt(II) complex. The true stoichiometry of this reaction was not established, because the oxidation mechanism of the cobalt ions remains unclear. It is difficult to study the synthesized compound by ^{1}H NMR spectroscopy because of many unresolved signals in spite of the diamagnetic character of the spectrum itself. It is most likely that the total spin multiplicity of complex **I** is equal to zero, since all cobalt(III) ions exist in the low-spin state, which is rather characteristic of this ion in this oxidation state.



Scheme 2.

The structure of synthesized complex **I** was confirmed by the XRD data (Fig. 1). According to the XRD data, ligand L in the complex is deprotonated over the nitrogen atom of the imidazole ring and two OH groups. The corresponding C–O bond lengths (1.327(13)–1.426(13) Å) fall onto the range of values characteristic of the ordinary bond C–O (1.38–1.42 Å) [24], which indicates the absence of the oxidized form of the ligand in the complex, since the C–O bonds are shorter in this case (1.28–1.30 Å) [10]. The $[(Bipy)_5Co_3(L)_2]^{3+}$ cation in the crystal of complex **I** occupies the partial position: the twofold axis passing through the central cobalt(III) ion (Co(2)) and the center of the N...N section in the bipyridine coordinated to this ion (Co–N 1.873(18) and 1.94(2) Å). The coordination environment of this ion is built up to an octahedral geometry by two nitrogen atoms of the imidazole ring (Co–N 1.930(7) Å) and two oxygen atoms of the C–O groups (Co–O 1.866(8) Å) of two ligands L. The so-called "symmetry measures" [25] describing the deviation of the geometry from an ideal octahedron (OC-6) confirm that the polyhedron shape is close to that of an octahedron. The lower the symmetry measures, the better the description of a polyhedron by the corresponding polygon. For the cobalt(III) ion (Co(2)), the octahedral symmetry measure S(OC-6) estimated from the XRD data using the Shape 2.1 program [25] is only 0.514 (Table 2). For comparison, the symmetry measure characterizing

Table 1. Main crystallographic data and refinement parameters for $[(Bipy)_5Co_3(L)_2](Cl)_3$ (**I**)

Parameter	Value
Empirical formula	$C_{88}H_{74}N_{14}O_4Cl_3Co_3$
FW	1674.75
T, K	100
Crystal system	Monoclinic
Space group	$C2/c$
Z	4
a, Å	22.697(7)
b, Å	24.612(7)
c, Å	20.932(7)
α, deg	90
β, deg	115.115(11)
γ, deg	90
V, Å^3	10588(6)
ρ_{calc}, g cm^{-3}	1.051
μ, cm^{-1}	5.87
$F(000)$	3456
$2\theta_{max}$, deg	50
Number of measured reflections	35869
Number of independent reflections	9262
Number of reflections with $I > 2\sigma(I)$	3445
Number of refined parameters	513
R_1	0.1263
wR_2	0.4203
GOOF	1.113
Residual electron density (min/max), e Å^{-3}	1.105/–1.047

the deviation of the polyhedron shape from one more ideal polygon with six vertices (trigonal prism (TR-6)) takes an appreciably higher value equal to 14.555 (Table 2).

The coordination environment of the second symmetrically independent cobalt(III) ion (Co(1)) is formed by four nitrogen atoms of two bipyridines (Co–N 1.909(10)–1.969(10) Å) and the nitrogen and oxygen atoms (Co–N 1.929(9), Co–O 1.896(8) Å) of one ligand L acting as the bridging ligand (Co...Co 5.833(2) Å). The shape of the formed coordination polyhedron differs slightly from an ideal octahedron. The octahedral and trigonal prismatic "symmetry measures" S(OC-6) and S(TP-6) are 0.310 and 15.500, respectively (Table 2).

According to the UV spectroscopy data, all metal ions exist in the same oxidation state (Fig. 2), which is confirmed by the absence of absorption bands induced by the charge transfer between the metal ions with different oxidation states [1]. The short-wavelength absorption bands (<368 nm) are induced by π–π* transitions in the biphenyl and phenol fragments of the ligand [26]. The longer-wavelength bands correspond to the transitions with a lower energy. In particular, the absorption bands at 475 and 661 nm correspond to the ligand-to-metal charge transfer (LMCT) and *d*–*d* transition in the metal ion, respectively [27].

The oxidation range of the cyclic voltammograms obtained for an acetonitrile solution of complex **I** containing tetrabutylammonium hexafluorophosphate as the supporting electrolyte contains no waves corresponding to any oxidation process. The reduction range (Fig. 3) contains one irreversible reduction wave with $E_{1/2} = -2.08$ V versus Fc/Fc$^+$ pair, which can be

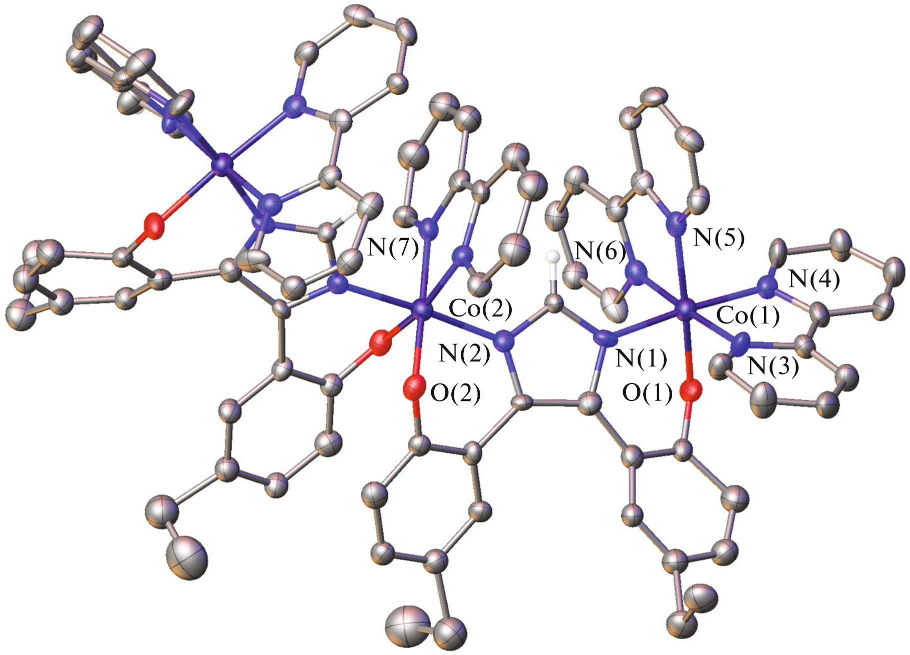


Fig. 1. General view of $[(\text{Bipy})_5\text{Co}_3(\text{L})_2]^{3+}$ cations in the crystal of complex **I** in the representation of atoms by thermal vibration ellipsoids ($p = 20\%$). Hydrogen atoms (except for the imidazole ring of ligand L) and minor components of the disordered ligands are omitted. The numeration is presented only for symmetrically independent metal ions and heteroatoms. The $[(\text{Bipy})_5\text{Co}_3(\text{L})_2]^{3+}$ cation in the crystal occupies the partial position: the twofold axis passing through the Co(2) ion and the center of the N...N section in bipyridine coordinated to this ion.

attributed to the Co(III)/Co(II) redox process resulting in the destabilization and decomposition of the complex. It is most likely that a similar destabilization also appears during the synthesis of complex **I** due to which the trinuclear cobalt(III) complex is the major reaction product rather than the binuclear cobalt(II) complex.

To conclude, we synthesized the new trinuclear cobalt(III) complex with 2,2'-(1*H*-imidazole-4,5-diyl)bis(4-ethylphenol). The study of the complex by XRD, CV, and UV-VIS spectroscopy showed that all cobalt ions had the oxidation state +3 and the complex formation reaction occurred with the oxidation of the initial cobalt(II) ions under action of the ligand. Thus, in spite of the capability of the ligand itself of oxidizing, the synthesized cobalt(III) complex demonstrates no ligand-centered oxidation processes characteristic of the dioxolene metal complexes.

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Table 2. Main geometric parameters* for complex **I** according to the XRD data obtained at 100 K

Parameter	Co(1)	Co(2)
Co–N(Py), Å	1.909(10)–1.969(10)	1.873(18), 1.94(2)
Co–N(L), Å	1.929(9)	1.930(7)
Co–O(L), Å	1.896(8)	1.866(8)
S(TP-6)	15.500	14.555
S(OC-6)	0.310	0.514

* The N(Py), N(L), and O(L) atoms correspond to the nitrogen atoms of bipyridine and the nitrogen and oxygen atoms of ligand L; S(TP-6) and S(OC-6) are deviations of the CoN_6 polyhedron from an ideal trigonal prism (TP-6) and an ideal octahedron (OC-6), respectively.

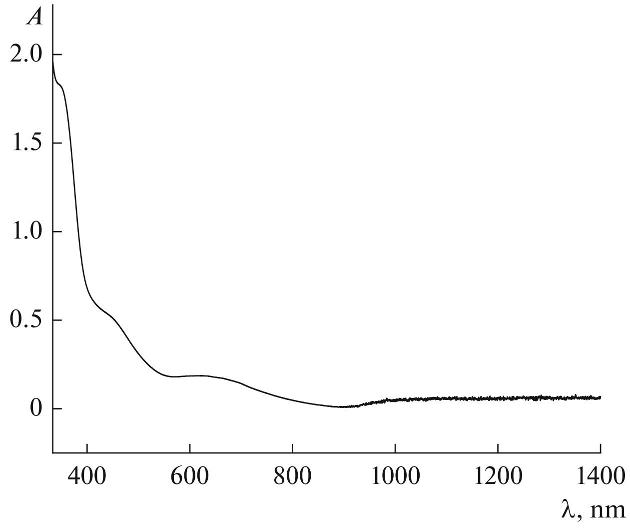

Fig. 2. UV-VIS spectrum of a 1 mM solution of complex **I** in acetonitrile.

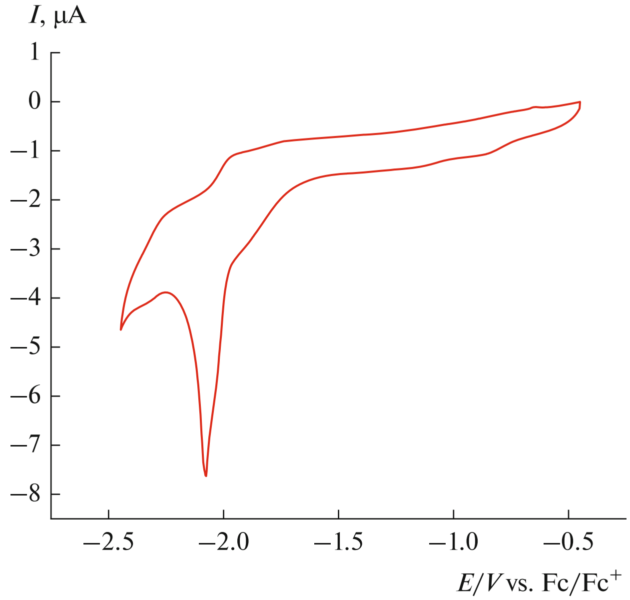

Fig. 3. Cyclic voltammogram of a 1 mM solution of complex **I** in acetonitrile in the reduction range ($c_{\mathrm{TBAPF_6}}$ = 0.1 M, potential sweep rate 100 mV/s, glassy carbon electrode 3 mm in diameter).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

ADDITIONAL INFORMATION

This article is prepared for the memorial issue in tribute to the Corresponding Member of the Russian Academy of Sciences K.Yu. Zhizhin on his 50th birthday.

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